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CITATION:

Shinohara, Hiroshi ...[et al]. Salt shell fallout during the ash eruption at the Nakadake crater, Aso volcano, Japan: evidence of an undergrounds hydrothermal system surrounding the erupting vent. Earth, Planets and Space 2018, 70: 46.

ISSUE DATE:

2018-03-20

URL:

<http://hdl.handle.net/2433/234502>

RIGHT:

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FRONTIER LETTER

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Salt shell fallout during the ash eruption at the Nakadake crater, Aso volcano, Japan: evidence of an underground hydrothermal system surrounding the erupting vent

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Abstract

A hot and acid crater lake is located in the Nakadake crater, Aso volcano, Japan. The volume of water in the lake decreases with increasing activity, drying out prior to the magmatic eruptions. Salt-rich materials of various shapes were observed, falling from the volcanic plume during the active periods. In May 2011, salt flakes fell from the gas plume emitted from an intense fumarole when the acid crater lake was almost dry. The chemical composition of these salt flakes was similar to those of the salts formed by the drying of the crater lake waters, suggesting that they originated from the crater lake water. The salt flakes are likely formed by the drying up of the crater lake water droplets sprayed into the plume by the fumarolic gas jet. In late 2014, the crater lake dried completely, followed by the magmatic eruptions with continuous ash eruptions and intermittent Strombolian explosions. Spherical hollow salt shells were observed on several occasions during and shortly after the weak ash eruptions. The chemical composition of the salt shells was similar to the salts formed by the drying of the crater lake water. The hollow structure of the shells suggests that they were formed by the heating of hydrothermal solution droplets suspended by a mixed stream of gas and ash in the plume. The salt shells suggest the existence of a hydrothermal system beneath the crater floor, even during the course of magmatic eruptions. Instability of the magmatic–hydrothermal interface can cause phreatomagmatic explosions, which often occur at the end of the eruptive phase of this volcano.

Keywords: Aso volcano, Hydrothermal system, Salt, Fallouts, Ash leachate, Volcanic eruption

Introduction

Volcanic lakes are efficient traps for volcanic volatiles and heat supplied from depth. The composition, temperature, or volume of water in the lakes are considered as indicators of the mass and energy budget of the magmatic–hydrothermal system (e.g., Delmelle and Bernard 2000; Pasternack and Varekamp 1997; Terada and Hashimoto 2017). Various types of eruptions occur at volcanic lakes, ranging from phreatic to magmatic. The eruptions at volcanic lakes are often associated with changes in

the balance of the magmatic–hydrothermal interactions (Rouwet and Morrissey 2015). Geochemical monitoring has revealed the nature and variation in the magmatic–hydrothermal interactions (e.g., Christenson et al. 2010; Rouwet et al. 2014).

The Nakadake cone of the Aso volcano, Japan, hosts a hot and acid crater lake and is one of the most active volcanoes in the country, with frequent phreatic to magmatic eruptions. The high levels of temperature and acidity indicate a large volcanic gas flux into the crater lake. Energy and material budget modeling of the crater lake revealed that more than half of the water in the lake is supplied through high-temperature volcanic fluids, and that more than half of the water is also lost by evaporation (Terada et al. 2012). Variation in volcanic activity has been observed with associated changes in the crater

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lake activity (Kawakatsu et al. 2000; Sudo et al. 2006). During the quiet period, the crater is filled by the lake water. With a decrease in the lake's water level, intermittent small phreatic eruptions begin to occur. After the lake has dried completely, high-temperature gas vents appear at the bottom of the crater, which then start to emit volcanic ashes. With a widening of the vent, the ash eruptions become continuous and intense and become associated with intermittent Strombolian activity. The crater lake waters recover with weakening the activity of magmatic eruptions. Phreatic–phreatomagmatic explosions often occur during and at the end of the eruption cycle (Ono et al. 1995; Sudo et al. 2006). Similar variations in volcanic activity and the surface manifestation of the crater lakes are observed in other volcanoes (Martínez et al. 2000; Rouwet and Morrissey 2015). The magmatic–hydrothermal interactions may control the correlation between the crater lake variations and the eruption cycle. However, the nature of the hydrothermal system during the absence of the crater lake is poorly known.

Recently, fallouts of salt-rich materials from the volcanic plume were observed during a high activity of the Nakadake crater, including during ash eruptions. We collected a few different types of the salt fallouts and report their occurrence, textural features and chemical compositions. The composition of the ash leachates and crater lake waters was also analyzed to compare with those of the salt fallouts. The origin of the salt fallouts precipitated during a period of crater lake absence is discussed, to understand the magmatic–hydrothermal interaction beneath the crater floor.

Aso volcano

The Aso volcano is one of the largest caldera volcanoes in the world, with the size of 25 km north–south and 18 km east–west diameter, and repeated gigantic pyroclastic flow eruptions from 270 to 90 ka. Several post-caldera cones, with compositions ranging from basalt to rhyolites, formed near the center of caldera after the last caldera-forming eruption (Ono and Watanabe 1985). The Nakadake cone is a stratocone with compositions ranging from basalt to basaltic-andesite and is the only active cone of the Aso volcano. During the past 6000 years, the dominant eruptive products at the Nakadake cone are black ash with some scoria, indicating that the foremost eruption style was that of continuous ash emission, that is called “ash eruption” (Ono et al. 1995). The Nakadake cone is currently quite active with repeated ash eruptions in 1974, 1979, 1984–1985, 1985–1995 and 2014–2015 (Ikebe et al. 2008; Ono et al. 1995; Yokoo and Miyabuchi 2015).

Another feature of the volcano is the hot and acid crater lake, located within the summit crater of the Nakadake cone. The crater lake is one of the hottest and most acidic crater lakes in the world, with water temperatures ranging from 40 to 80 °C and a pH level between -1 and $+1$ (Ohsawa et al. 2003, 2010; Miyabuchi and Terada 2009). The crater lake water submerges the crater bottom during a quiet period, and the water level decreases with an increase in the volcanic activity (Kawakatsu et al. 2000; Sudo et al. 2006). The bottom of Nakadake crater was filled with the crater lake water until 2009 (Shinohara et al. 2015), and the water volume decreased to almost zero in late 2011, when a few small phreatic eruptions occurred. The water volume recovered in 2012 and then decreased again to almost zero in late 2013 following several small phreatic eruptions. The crater bottom became hotter, and the incandescence was observed even in the daylight on November 18, 2014. The eruption started from the high-temperature vent on November 25, becoming more intensive with the enlargement of the vent (Yokoo and Miyabuchi. 2015). The eruption style was the continuous ash eruption with sporadic Strombolian activity, similar to past eruptions. The ash eruption culminated in late January, discharging $\sim 2 \times 10^6$ tons of ash until February 2, 2015 (Yokoo and Miyabuchi 2015; Marumoto et al. 2017). The eruption continued with some temporal pauses until May 21, 2015.

Observation of fallouts

Various non-silicate (salt) fallouts were observed at the Aso volcano during periods when the crater lake had almost or completely disappeared. The salt fallouts were first identified in May 2011, when the crater lake had almost dried out and a brownish plume emitted from a high-temperature vent of 585 °C at the center of the crater bottom. A small amount of water remained, surrounding the high-temperature vent (Fig. 1a). The salt-rich materials of a flaky shape fell from the plume and were deposited on the flank. The fallouts are yellowish-gray flakes, several mm in width, hereafter referred to as “salt flakes” (Fig. 1b). Salt flakes are fragile and are for the most part water-soluble. The brownish color of the plume is likely induced by the salt flakes. The salt flakes were observed on May 18, 19, and 31, 2011, and June 6, of the same year by people visiting the crater rim on the leeward side of the plume. Although the fallouts were observed only on limited occasions, the salt flakes are likely released for 2 weeks since the emission of the brownish plume was continuously observed from mid-May to early June. Eruptions and significant ash falls were not observed during this period.

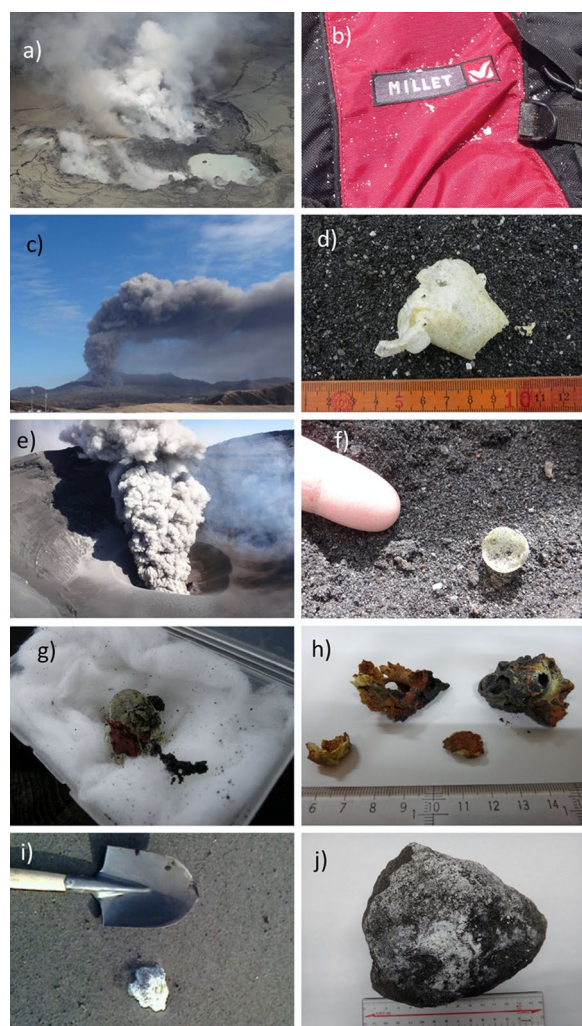


Fig. 1 Photographs of the activities and salt fallouts. **a** The crater bottom on May 19, 2011. The crater lake is almost dried out, presenting a brownish plume emitted from a high-temperature vent at the center of the crater bottom. Several other vents also emitted gases intensively. Small amounts of crater lake water remained around the vents. **b** The salt flakes settled on a backpack on May 19, 2011, at the leeward side of the plume toward the northern rim of the crater. **c** Ash eruption on January 13, 2015. **d** A salt shell observed on the ground on January 13, 2015. **e** The ash eruption on March 17, 2015. **f** A salt shell fallen from the gas plume 1 h after the temporal cessation of the ash eruption on March 17, 2015. **g** The salt shells collected on March 17, 2015, and stored in a box. The salts seem to be partly dissolved due to atmospheric moisture and partly recrystallized. **h** The salt lumps collected on March 26, 2015. **i** A bomb covered in fine white salts, found on December 27, 2014. **j** A close-up of the bomb in the laboratory. Most of the salts were fell off during transport because the salts are very fragile

The salt fallouts of different shapes were observed several times during the eruptive period of 2014–2015. The salts were discharged with the ashes during an ash eruption on January 13, 2015 (Fig. 1c). The salt fallouts

had a hollow yellowish-white-colored shell structure, with a maximum size of ~ 5 cm, hereafter referred to as “salt shell” (Fig. 1d). The shells were thin and fragile, commonly occurring round, elongated, or coalesced round shapes. On March 17 and 20, 2015, the salts were released from the gas plume approximately 1 h after the temporal cease of the weak ash eruption (Fig. 1e). These fallouts were hollow, fragile, spherical shells of a yellowish-white color, with a maximum size of ~ 1 cm (Fig. 1f). The shape and color of these salt shells were quite similar to the hollow sulfur spherules observed at several acid crater lakes such as Kusatsu-Shirane and Poás volcanoes (Ohashi 1919; Oppenheimer and Stevenson 1989; Takano et al. 1994). These salt shells, however, were for most part water-soluble and not sulfur spherules. They absorb moisture and were recrystallized into a denser structure after being stored in a box that was not sealed against the moisture (Fig. 1g). On March 26, 2015, similar dense salt materials (hereafter referred to as “salt lump”), a few cm in size, were found on the ground (Fig. 1h). These salt lumps look similar to the recrystallized salt shells. A volcanic bomb covered with salts of a white color (hereafter referred to as “white salt”) was found on the eastern flank, ~ 300 m from the vent, on December 27, 2014, after the occurrence of Strombolian activities (Fig. 1i). The salts covering the bomb were a layer of fine fibers, of a few mm in length (Fig. 1j). The bomb appeared porous and consisted of consolidated tuff without signs of a significant hydrothermal alteration. The bomb is less likely the product of the Strombolian activity, as it is likely to be a block of the non-juvenile lithics beneath the crater floor, which was ejected by the associated explosions. A bomb with the white salts was only found on this occasion.

Analytical method

All the salt materials, including the salt flakes, the salt shells, the salt lumps, and the white salts, were analyzed. In order to evaluate the origin of the salt materials, the composition of the crater lake waters and leachate of the ashes emitted by the ash eruptions was also analyzed. The water-soluble components were analyzed using ion chromatography, and the bulk composition was measured through energy-dispersive X-ray spectrometry (EDS). For the analyses of the water-soluble components, the salt materials were dissolved in pure water and filtered through a $0.45\text{-}\mu\text{m}$ membrane filter, diluted, and analyzed without any further pre-treatment. Some solid materials, such as mineral and rock fragments, and elemental sulfur, remained settled after dissolution in the pure water. The concentrations of F, Cl, SO_4 , Na, K, Mg, and Ca were determined. Fluoride forms complex chemical compounds under conditions of high Fe and Al content; therefore, the results of the F analyses of the crater

lake waters by the ion chromatography are not accurate (Takano et al. 2000). An EDS (Oxford X-Max 20) on a scanning electron microscope (JEOL JSM6610LV) was used for the chemical composition analysis on the surface of the salt grains. Fragments of the salt samples were attached to an aluminum plate with double-side carbon tape and were then coated by graphite. Because the salt sample cannot be polished, only flat and smooth surfaces that could be oriented perpendicular to the microprobe were selected for analysis. The acceleration voltage of the electron microprobe was 15 kV, and the probe current was ~ 1 nA. The X-ray signal lower than 10 keV was analyzed.

Crater lake water samples were collected using the same method employed by Miyabuchi and Terada (2009). Chemical analyses of the lake water samples were performed by the Chikyu Kagaku Kenkyusho Co., Ltd (Nagoya, Japan). Concentrations of F, Cl, and SO_4 were determined using ion chromatography, SiO_2 was analyzed through a molecular absorption spectrometry method, and the cation concentrations were measured by an atomic absorption spectroscopy technique. The crater lake waters are very acidic, and some components, such as HCl, are likely lost through evaporation (Shinohara et al. 2015; Capaccioni et al. 2016). In order to examine the effect of the evaporation, the crater lake water was dried overnight at 90 °C, and the dried material was then dissolved in pure water and analyzed using the same ion chromatography method as was used for the salt materials.

Water-soluble components of the volcanic ashes emitted in 2014–2015 were analyzed. The ashes, collected shortly after the deposition on a clean surface, were used for the analyses. These ashes were mixed with pure water by 1:50 weight ratio and agitated for about 60 min at a temperature of ~ 40 °C in an ultrasonic bath, shaken intermittently. The solution was filtered using a 0.45- μm membrane filter after decantation and analyzed for the anions and cations using the ion chromatography method (Witham et al. 2005).

Results

The crater lake of the Aso volcano is a hyper-saline acid crater lake, and its composition varies with the lake volume, temperature, and volcanic activity (Ohsawa et al. 2003, 2010; Terada et al. 2012). Absolute concentrations of the dissolved species are variable. During 2008–2012, the measured sulfate concentration in the lake water varied between 40,000 and 130,000 ppm (Table 1). In contrast, the relative concentrations of the dissolved species were fairly constant (Fig. 2a). Concentrations of SiO_2 and Ca are variable, likely due to the precipitation of gypsum and silica, which is a common process in hyper-saline

lake waters (Varekamp et al. 2000). The composition of the dried crater lake water samples was almost identical to their original lake water compositions, except for low Cl contents. This likely indicates that the evaporation only removes the HCl, whereas other anions, such as F and S, remain as salts. Ashes contain quite variable amounts of water-soluble materials; e.g., the SO_4 concentrations range from 400 to 110,000 ppm (Table 1). Compositions of the ash leachate are variable, but have large SO_4/Cl and Na/K ratios, similar to the dried crater lake water samples (Table 1 and Fig. 2b). In contrast, the ash leachates have distinctly different composition than the crater lake waters and their dried samples, with larger Ca/Na and smaller Mg/Na ratios. The higher Ca concentrations are accompanied by a high SO_4 concentration, with the Ca/ SO_4 molar ratio being approximately one. This agrees with the common feature in ash leachates where a majority of the salt on ashes likely presents as CaSO_4 and NaCl (Witham et al. 2005).

The dissolved salt fallouts analyzed by ion chromatography are rich in F, Cl, SO_4 , Na, and Mg, with an exception of the white salt, which is almost pure NaCl (Table 1 and Fig. 2c). Compositions of the dissolved salt flakes, shells and lumps are similar to those of the dried lake water samples, with large Mg/Na ratios (close to one), and variable but small Ca/Na ratios (smaller than one). The salt flakes emitted in 2011 have almost identical composition to the dried lake water samples. The salt shells and lumps emitted during the eruptive stage in 2015 have smaller SO_4/Na and Ca/Na ratios and larger Cl/Na ratios than those of the salt flakes. The salt shells and lumps have similar composition. The compositions of the salt fallouts, as measured by the EDS analysis, are quite variable even when different spots on the same sample were analyzed. A $10 \times 10 \mu\text{m}$ area is analyzed using the EDS, and the large observed variation indicates a heterogeneous composition, likely due to the distribution of non-water-soluble particles such as fragments of mineral and rock fragments.

Discussion

Emission of water-soluble salts from volcanoes is not rare. Volcanic ashes commonly contain water-soluble salts (ash leachates) with variable contents (Witham et al. 2005). Water-soluble salts, such as NaCl and KCl, are often found in the high-temperature fumarolic sublimates (Symonds 1993; Africano et al. 2002). However, the observation of the salt fallouts from a plume is an uncommon phenomenon, particularly from an ash plume. This study is the first report of such a case, as far as the authors know. Compositions of the salt fallouts, with the exception of white salt, are similar to the dried lake water samples, indicating the salt fallouts formation

Table 1 Composition of ash leachate, salt materials, crater lake water, and dried crater lake water

Sample type	Sample no.	Sampling date (yyyy/mm/dd)	Temp [#] (°C)	Method	F (mg/kg)	Cl (mg/kg)	SO ₄ (mg/kg)	Na (mg/kg)	K (mg/kg)	Mg (mg/kg)	Ca (mg/kg)	SiO ₂ (mg/kg)	T-Fe ^s (mg/kg)	Al (mg/kg)
Salt flake ^a	S110518-0	2011-5-18		IC	36,794	25,631	317,641	17,380	2891	18,865	24,779			
Salt flake ^a	S150518-1	2011-5-18		IC	47,451	12,327	353,902	19,231	1700	23,934	11,192			
Salt flake ^a	S110518-2	2011-5-18		IC	41,905	17,146	358,306	18,966	1807	24,249	12,753			
Salt flake ^a	S110519	2011-5-19		IC	46,032	16,541	391,964	20,195	3173	27,072	6898			
White salt ^a	S141227	2014-12-27		IC	4186	527,412	13,325	327,602	4288	311	1718			
Salt shell ^a	S150113	2015-1-13		IC	36,125	46,002	255,798	21,356	3765	19,072	1707			
Salt shell ^a	S150317	2015-3-17		IC	26,174	75,124	163,225	22,620	3270	23,130	4988			
Salt shell ^a	S150320	2015-3-20		IC	25,089	83,026	191,171	19,636	2563	26,858	881			
Salt lump ^a	S150327	2015-3-27		IC	34,630	106,140	311,211	25,457	4260	42,280	751			
Salt flake ^a	S110518-0	2011-5-18		EDS	46,300	35,200	635,577*	21,700	15,400	24,700	12,900	34,435	87,700	71,100
Salt shell ^a	S150113	2015-1-13		EDS	19,500	32,000	298,479*	12,000	44,300	14,700	18,400	98,384	282,700	47,700
Salt shell ^a	S150113	2015-1-13		EDS	13,900	39,900	381,107*	10,300	50,800	15,800	7000	23,741	281,100	40,000
Salt shell ^a	S150113	2015-1-13		EDS	20,800	42,000	381,406*	11,100	48,400	19,500	4600	16,469	213,300	42,600
Salt shell ^a	S150113	2015-1-13		EDS	15,500	72,200	391,585*	37,100	28,800	54,900	5000	24,596	149,700	27,900
Salt shell ^a	S150113	2015-1-13		EDS	13,000	39,700	351,768*	10,400	50,000	16,000	12,500	34,435	274,100	40,500
Salt shell ^a	S150113	2015-1-13		EDS	12,500	133,300	322,728*	74,800	34,200	18,300	0	7914	209,600	34,700
Salt shell ^a	S150113	2015-1-13		EDS	29,000	34,200	362,246*	9400	38,700	16,100	0	18,607	204,400	46,200
Salt shell ^a	S150113	2015-1-13		EDS	0	43,500	386,196*	10,100	49,100	19,900	0	9197	218,700	41,400
Salt shell ^a	S150317	2015-3-17		EDS	143,800	13,000	380,807*	10,300	500	3800	1400	10,694	11,800	102,700
Salt shell ^a	S150317	2015-3-17		EDS	64,500	91,300	272,433*	30,700	5900	52,200	3400	27,163	116,500	34,800
Salt shell ^a	S150317	2015-3-17		EDS	46,900	73,600	237,705*	24,900	8100	39,300	7600	75,072	119,500	36,300
Salt shell ^a	S150317	2015-3-17		EDS	55,700	106,200	312,250*	30,400	6600	55,000	5900	42,990	159,300	39,500
Lake water ^b	LW080704 ⁺	2008-7-4	71.6	IAM	5790	38,000	59,700	2410	903	3010	1810	363	4920	6880
Lake water ^b	LW090212	2009-2-12	56.4	IAM	6550	44,300	66,700	2740	1060	3540	1970	344	5860	8430
Lake water ^b	LW090324	2009-3-24	60.0	IAM	6928	46,944	74,408	2920	1128	3592	3208	348	6464	8640
Lake water ^b	LW100825	2010-8-25	79.1	IAM	13,700	60,600	131,000	5520	2650	7120	300	435	10,600	17,400
Lake water ^b	LW111206	2011-12-6	61.8	IAM	5180	22,499	40,600	1982	732	2849	1184	530	3460	4640
Lake water ^b	LW120329	2012-3-29	71.7	IAM	7670	36,000	62,400	2720	1120	3690	1130	580	5020	7690
Lake water ^c	LW100825A	2010-8-25		IC	15,722	76,632	160,077	7707	5945	9393	2465			
Lake water ^c	LW111206A	2011-12-6		IC	5500	24,249	45,970	2204	1272	2934	1662			
Lake water ^c	LW120329A	2012-3-29		IC	8702	41,721	74,972	3323	2256	4194	1957			
Dried LW ^d	LW100825B	2010-8-25		IC	16,162	18,778	166,096	8029	5599	9637	2420			
Dried LW ^d	LW111206B	2011-12-6		IC	5411	3691	46,466	2365	1400	2951	1790			
Dried LW ^d	LW120329B	2012-3-29		IC	8689	3944	75,141	3413	2234	4210	1999			

Table 1 continued

Sample type	Sample no.	Sampling date (yyyy/mm/dd)	Temp ^a (°C)	Method	F (mg/kg)	Cl (mg/kg)	SO ₄ (mg/kg)	Na (mg/kg)	K (mg/kg)	Mg (mg/kg)	Ca (mg/kg)	SiO ₂ (mg/kg)	T-Fe [§] (mg/kg)	Al (mg/kg)
Ash leachate ^e	Ash141127	2014-11-27		IC	375	175	1481	257	32	43	798			
Ash leachate ^e	Ash141210	2014-12-10		IC	63	95	924	131	5	32	381			
Ash leachate ^e	Ash151112	2015-1-12		IC	155	452	1367	273	39	83	525			
Ash leachate ^e	Ash150113	2015-1-13		IC	144	334	3649	417	59	183	992			
Ash leachate ^e	Ash150223	2015-2-23		IC	600	445	3008	588	49	199	1069			
Ash leachate ^e	Ash150224	2015-2-24		IC	776	279	4212	472	86	264	1325			
Ash leachate ^e	Ash150225a	2015-2-25		IC	224	207	5242	336	56	320	1322			
Ash leachate ^e	Ash150225b	2015-2-25		IC	285	387	6164	487	115	307	1473			
Ash leachate ^e	Ash150317	2015-3-17		IC	305	210	1176	221	24	60	615			
Ash leachate ^e	Ash150320a	2015-3-20		IC	204	84	376	174	17	42	177			
Ash leachate ^e	Ash150320b	2015-3-20		IC	152	383	2234	314	47	126	714			
Ash leachate ^e	Ash150320c	2015-3-20		IC	437	923	5960	504	123	263	2044			
Ash leachate ^e	Ash150221	2015-3-21		IC	3419	5335	69354	2402	269	1865	18,605			
Ash leachate ^e	Ash150429	2015-4-29		IC	188	241	982	200	18	83	408			

IC ion chromatography, IAA ion chromatography + atomic absorption spectroscopy + molecular absorption spectroscopy, EDS energy-dispersive X-ray spectroscopy. Multiple spots of the same sample were analyzed by EDS, and the data of each spot are listed

Blank cell: no data, 0: not detected, #: temperature of the lake, §: total Fe, *: S wt. % obtained by the EDS analyses are recalculated as the weight % of SO₄, +: data cited from Miyabuchi and Terada (2009)

^a Concentrations are calculated relative to the whole sale materials including insoluble components

^b Concentration in water sample

^c Re-analyses of the stored sample. Concentration in water sample

^d Dried lake water samples are dissolved in pure water of the original volume

^e Concentrations are calculated relative to the ash weight

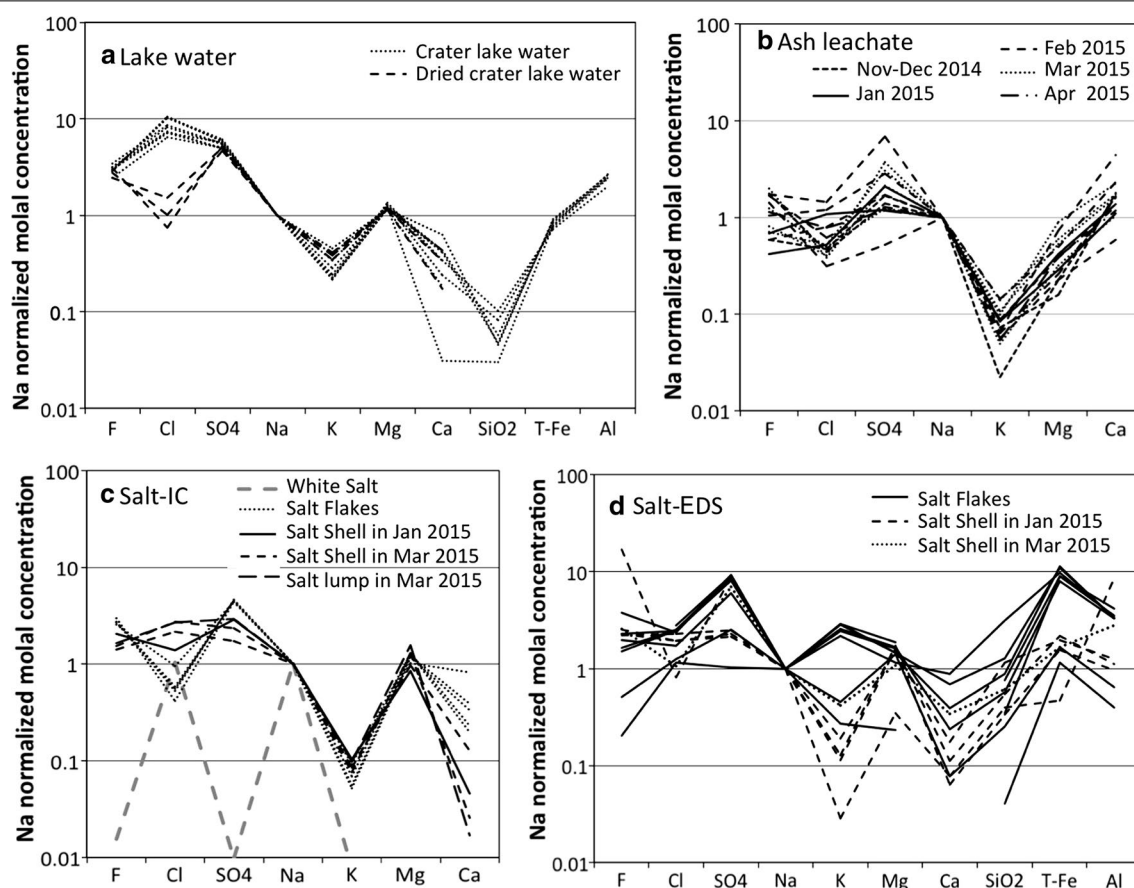


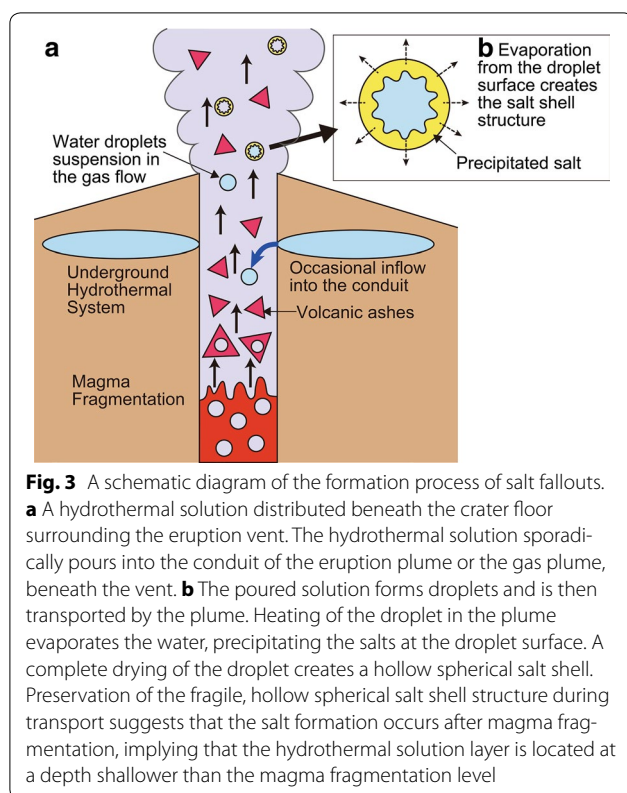
Fig. 2 Composition of the salt fallouts, ash leachates, crater lake waters, and dried samples of the crater lake waters (Table 1). The Na-normalized molal concentrations of each species are plotted. **a** Composition of the crater lake waters and of the dried samples of the crater lake waters. **b** Composition of the ash leachates. **c** Composition of the salt fallouts obtained by an ion chromatography analysis. **d** Composition of the salt fallouts obtained by an EDS analysis

caused by the evaporation of the lake water. The salt fallouts have large Mg/Na ratios (close to one), similar to the ratios observed from the dried lake water samples, but different from the ash leachates. Although there are no samples of the fumarolic sublimates at Aso volcano, such sublimates rarely contain Mg-containing salts (Symonds 1993; Africano et al. 2002). The Mg-rich composition of the salt fallouts is different from the Mg-poor fumarolic sublimates.

The salt flakes were observed when a brown-colored plume emitted from a high-temperature vent, surrounded by the remnant of the crater lake (Fig. 1a). The salt flakes are likely formed by evaporation of the crater lake water sprayed from the vent, which caused the brown color observed in the plume. The compositions of the salt shells and lumps are also similar to the crater lake water, indicating that these salts were formed by evaporation of hydrothermal fluids, similar to the crater lake water. The salt shells and lumps were observed

during a period when the crater lake did not exist on the surface (Fig. 1c, e). The hydrothermal fluids forming the salt shells and lumps need to be derived from an underground hydrothermal system surrounding the erupting vent (Fig. 3a).

The salt shells, particularly those from of March 2015, have the fairly specific structure of a hollow spherule with a thin shell (Fig. 1f). This structure resembles the hollow sulfur spherules floating on other crater lakes (Ohashi 1919; Takano et al. 1994). Ohashi (1919) proposed that sulfur spherules are formed by the upward passage of gas bubbles through liquid sulfur pools at the bottom of the crater lakes. By analogy, gas bubbles passing through a liquid salt pool can create the salt spherules. In contrast to the common occurrence of elemental sulfur in the fumarolic fields, massive deposits of salts are rarely observed in active volcanoes, and the salt spherule formation at a liquid salt pool is rendered less likely.



The hollow structure of the salt shells can be formed by evaporation of droplets of hydrothermal solution during their transportation within the plume. The hydrothermal solutions pour into the plume forming droplets, which then are transported in the plume by a flow stream of gas–ash mixture. The droplets are heated in the plume, because plume temperature is likely much higher than that of the hydrothermal system. Heating of the droplets causes the water to evaporate and the salt to precipitate at the droplet surface, forming the salt shells, and the complete drying of the droplet makes these shells hollow (Fig. 3b). A thin shell implies that the salt volume was much smaller than the droplet volume. The crater lake water contains 8–25 wt.% of dissolved solids (Table 1). If we assume that the densities of the crater lake water and the precipitated solids are 1.0 and 2.5 (g/cm³), respectively, the precipitated salt volume is estimated to be 3.2–10 vol.% of the original droplet, requiring the shell thickness to be 0.01–0.03 times the droplet radius. The estimated thickness of a shell with a 5 mm radius is 0.05–0.15 mm. Although no quantitative measurements for the volume and weight ratios of the salt shells were conducted, these estimates look reasonable from the appearance (Fig. 1f). Preservation of the fragile structure of the hollow shells during the transport indicates that the salt shells were not damaged by any strong turbulent flows with ashes, and that the salt formation

occurred after the magma fragmentation. A hydrothermal solution layer is likely located near the surface, at a depth shallower than the magma fragmentation level.

Formation of salt shells requires subtle conditions of hydrothermal solution flowing into a hot gas or eruption plume, but can occur at other crater lake bearing volcanoes, such as the Poás and the Copahue volcanoes. The salt fallouts, however, will not be preserved for a long time, as these will easily be crushed to a powder and get blown away or get dissolved by rain water. The salt fallouts can be observed only by frequent examinations at the crater rim on the leeward of the plume during eruptions or active degassing. Such examinations, however, can be risky. The rim of the Nakadake crater is easily accessible by road, enabling frequent exploration of the crater rim with a low risk, even during the active stages. This frequent monitoring has made the observation of rare salt fallouts possible at the Nakadake crater.

Compositions of the salt flakes collected in 2011 are almost identical to those of the dried crater lake water samples (Fig. 2). Compositions of the salt shells and lumps collected in March 2015 are similar to, but have larger Cl/SO₄ ratios than, the salt flakes. The salt shells and lumps have an identical composition which indicates that the salt lumps are recrystallized materials from the salt shells. The salt shells collected in January 2015 have an intermediate Cl/SO₄ ratio of the salts than those collected in 2011 and March 2015, suggesting a gradual increase in the Cl/SO₄ ratios with time. The salt shells are likely derived from the subsurface hydrothermal solutions. The temporal increase in Cl/SO₄ ratios can be caused by gradual changes in the hydrothermal solution composition under the subsurface conditions. However, no evidence of the composition of subsurface hydrothermal solutions currently exists, and the cause for compositional variation of the salt fallouts remains unclear.

The origin of the white salts, with an almost purely NaCl composition, is also unclear. The salts have a fibrous texture covering the bomb surface. Such a fibrous texture resembles that of a fumarolic sublimate precipitated from a vapor, such as fibrous sulfur. High-temperature fumarolic gases contain a relatively high concentration of Na, approximately 10–100 ppm at 800–900 °C (Hedenquist et al. 1994; Taran et al. 1995), which sublimates as NaCl by cooling. The fumarolic sublimates, however, are not pure NaCl but a mixture of various species depending on the sublimation temperature (Symonds 1993; Africano et al. 2002). The lack of the alteration on the bombs does not suggest a high-temperature origin for the white salts. Similar fibrous salt textures can be found also on rocks through which the seawater slowly seeps out at warm conditions (Murakami 1999). If a porous bomb contained a salt solution, a fibrous salt can form from the salt solution

seeping out from the interior through warming by the sunshine. The NaCl-rich composition is a feature of neutral chloride waters commonly found in mature geothermal systems (Giggenbach 1996). Large Na/K ratios can be obtained under low-temperature equilibrium conditions (Giggenbach 1988). The NaCl-rich salt can form from a mature low-temperature equilibrated hydrothermal solution. If the white salt is derived from such a neutral pH solution, this neutral pH solution would be distributed by the acidic hydrothermal system and the erupting vent, implying a heterogeneous and complex structure of the magmatic–hydrothermal interface.

The difference in the ash leachate compositions compared to those of the salt fallouts and the crater lake water indicate that the salt components of the ashes are not derived from the hydrothermal solution, but rather from magma degassing. Several ash samples were collected on the same day of the salt shell collection, such as January 13, March 17, and March 20, 2015 (Table 1). Even these ash samples have larger Ca/Na and smaller Mg/Na ratios than the salt shells, suggesting that the contribution of the salt shell components to the ash leachate is not significant. The absence of any hydrothermal components in the ash leachate indicates that the hydrothermal solution fed into the erupting or degassing conduit was not continuous and likely infrequent.

Instability of the magmatic–hydrothermal interface may cause phreatomagmatic eruptions (Morrissey et al. 2000). Phreatic or phreatomagmatic explosions are a common feature at the end of the eruption cycles of the Aso volcano (Sudo et al. 2006). During the continuous ash eruptions, from November 2014 to May 2015, phreatic to phreatomagmatic eruptions did not occur and the interface seemed stable. The occasional hydrothermal solution input to the degassing conduit, forming the salt fallouts, did not cause further perturbation of the interface. The southern part of the crater floor, 100 m wide, suddenly subsided by 50 m on May 3, 2015, without any significant eruptive activity. The frequency and intensity of the ash eruptions decreased thereafter, and the eruption ceased on May 21, 2015. The crater lake water subsequently recovered by June 6, 2015. The immediate recovery of the crater lake is consistent with the continuous existence of a hydrothermal system.

The lack of phreatomagmatic explosion during the recent eruption cycle (2014–2015) suggests that the magmatic–hydrothermal interface has remained stable in this case. During the eruption periods of 1984–1985 and 1989–1991, frequent phreatomagmatic explosions occurred during the late stages, followed shortly by a crater lake recovery. Ono et al. (1995) suggested that these

processes can be caused by water from a heavy precipitation. However, the continuing existence of a hydrothermal system surrounding the eruptive vent provides a condition for spontaneous phreatomagmatic explosions at the Aso volcano, with possible instability at the magmatic–hydrothermal interface occurring even during a continuous magmatic eruption, without any heavy precipitation.

Summary

Various salt fallouts were observed during the intensive gas emission and ash eruption stages of the Nakadake crater of the Aso volcano. Chemical compositions of the salt fallouts were analyzed and compared to those of the ash leachates, the crater lake waters, and the dried samples of the crater lake water. Most of the salt fallouts have composition similar to those of the dried crater lake water samples and are quite different from those of the ash leachates. Flakes of salts were observed in May 2011 when only a small volume of the acid crater lake water remained, and a brownish plume intensively emitted from a high-temperature vent. The chemical composition indicates that the salt flakes are likely formed by the evaporation of the crater lake water sprayed by the fumarolic jet. Hollow spherical salt shells were observed at several times during the eruptive stage of 2014–2015, when the ash eruption with intermittent Strombolian explosions continued with temporal pauses. The salts are released from the plume during weak ash eruptions or shortly after the temporal cessation of the ash eruptions. Although the crater lake completely dried up prior to the eruptive stage, the similarity in chemical composition suggests that the shell salts are also formed by the evaporation of an underground hydrothermal solution pouring into the conduit of a volcanic plume. The hollow structure suggests that the salts were formed by the heating of hydrothermal solution droplets suspended in the plume stream. The preservation of the fragile hollow shell structure, even after transport by the plume, suggests that the hydrothermal solution pours into the conduit at a shallow depth well above the level of magma fragmentation. The salt shells indicate a close distribution of the hydrothermal system surrounding the erupting vent, even during the continuous magmatic eruption stage. The perturbation of the magmatic–hydrothermal interface can cause phreatomagmatic explosions, which, at this volcano, often occur at the end of an eruptive period.

Abbreviation

EDS: energy-dispersive X-ray spectrometry.

Authors' contributions

HS performed chemical analyses of salts, ash leachate, and lake waters and led the discussion. NG performed EDS analyses of the salts. AY and TO performed detailed observation of the volcanic activity including the salt fallout occurrences. AT performed collected the crater lake waters and performed their analyses. All authors contributed to discussion and preparation of the manuscript. All authors read and approved the final manuscript.

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Acknowledgements

We thank Drs. T. Kagiya, M. Utsugi, S. Yoshikawa, H. Inoue, R. Kazahaya, and Y. Miyabuchi for their supports during the fieldwork, Japan Meteorological Agency for offering some of the salt fallouts samples, and Ms. M. Someya for sample analyses. We appreciate Drs. Accocella and Rouwet and an anonymous reviewer for their constructive comments, which significantly improved the manuscript.

Competing interests

The authors declare that they have no competing interests.

Ethics approval and consent to participate

Not applicable.

Funding

This work is partially supported by Grants-in-Aid for Scientific Research (KAKENHI) 22340130, 25287115, and 17H02955 from the Japan Society for the Promotion of Science (JSPS) to HS.

Publisher's Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Received: 1 September 2017 Accepted: 6 February 2018

Published online: 20 March 2018

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